#### UNIVERSITY OF SASKATCHEWAN DEPARTMENT OF CHEMISTRY CHEMISTRY 111.3 FINAL EXAMINATION

-April, .	1997	NAME:
	· _	please print legibly!
Time:	3 hours	SIGNATURE:
		STUDENT NO .:
Please i	indicate your Section:	
02 Re:	id MWF 9:30	C10 Walker (Melfort)
	anski T Th 10:00	

# INSTRUCTIONS:

- 1. This examination consists of 16 pages including a data sheet. Please ensure your paper is complete.
- Answer all questions on the examination paper. For multiple choice questions, circle the correct answer on the examination paper and enter the answer on the blue optical scan sheet by filling in the appropriate circle with a dark pencil.
- 3. Complete the information required (name etc.) at the top of the optical scan sheet. Your Student Number is to be coded onto the upper left portion of the sheet reading downward. Note that the numbers in the code spots read from zero through nine as you read from left to right ... i.e. the first spot is 0, not 1.
- Show your work in problem solutions. Ensure that your answer has the appropriate units and number of significant figures.
- 5. This is a closed book examination. The marks for each question are indicated. Total marks are 160. Allowing for reading the questions and checking over, this is 1 mark per minute; apportion your time accordingly.

### Additional Information:

$$K_w = 1.00 \times 10^{-14} \text{ at } 25 \text{ °C}$$
  $\Delta E = E^o - \frac{0.0592}{n} \log_{10}Q \text{ at } 25 \text{ °C}$  (Nernst Equation)

Question	Maximum Marks	Marks Awarded
1-25	50	and the
26-31	30	
32	20	
33	5	
34	5	r
35	10	
36	10	
37	10	
38	15	
39	5	
Total	160	

I.	Multiple	Choice	(2	marks	each)
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1. Identify the substance reduced in the reaction,

 $PbO_2(s) + SO_4^2(aq) + 4 H'(aq) + 2 Hg(\ell) + 2 Cl'(aq) \rightarrow Hg_2Cl_2(s) + PbSO_4(s) + 2 H_2O(\ell)$ 

- A. PbO,
- B. SO,2-
- C. Hg
- D. H
- E. none of these

2. If an acid has  $K_a = 4.93 \times 10^{-10}$ , then  $K_a$  for its conjugate base is

- A. 9.95 x 10-8
- B. 5.17 x 10 1
- C. 5.17 x 10-10
- D. 2.03 x 10-3
- E. 2.03 x 10°

 The dissolution of calcium nitrate in water is an exothermic process. If the temperature is decreased from 75°C to 60°C, the solubility of calcium nitrate in water should

- A. increase
- B. decrease
- C. not change
- D. change, but cannot predict how without more information

4. When SO,2 is converted to S2, \_\_\_\_ electrons are \_\_\_\_ by each sulfur atom.

- A. 0, lost or gained
- B. 2, gained
- C. 6, lost
- D. 6, gained
- E. 8, gained

5. Molarity is defined as:

- A. Moles of solute per kilogram of solution
- B. Moles of solute per litte of solvent
- C. Moles of solute per kilogram of solvent
- D. Moles of solute per mole of solution
- E. None of the above

- 6. For an aqueous solution at 25°C, if [H<sub>3</sub>O\*] = 0.050 mol L-1, then [OH-] =
  - A. 2.0 x 10<sup>-6</sup> mol L<sup>-1</sup>
  - B. 5.0 x 10<sup>-2</sup> mol L<sup>-1</sup>
  - C. 2.0 x 10<sup>-12</sup> mol L<sup>-1</sup>
  - D. 1.0 x 10-7 mol L-1
  - E. none of these
- 7. The following standard reduction potentials are valid for aqueous solutions at 25°C.

Reduction Half-Reaction	Standard Reduction Potentials E* (V)	
$Hg^2 + 2e^- \rightarrow Hg$	0.851	
Ag + e - Ag	0.800	
$Fe^{3+} + e^{-} \rightarrow Fe^{3+}$	0.770	
Cu² + 2 t → Cu	0.340	
$Sn^{2*} + 2e^{-} \rightarrow Sn$	-0.136	
$Ni^{2^{*}} + 2e^{-} \rightarrow Ni$	-0.230	
Fe2 + 2 e → Fe	-0.409	
$Zn^{2*} + 2e^- \rightarrow Zn$	-0.763	
Al"+3e" -> Al	-1.706	

From the E\* values tabulated above, an element or ion which will oxidize tin but will not oxidize silver is

- A. Al
- B. Zn3\*
- C. Fe3
- D. Hg
- E. On3\*
- 8. Which of the following aqueous solutions has the lowest freezing point?
  - A. pure water
  - B. 0.1 mol kg- KBr
  - C. 0.1 mol kg-1 CaCl,
  - D. 0.1 mol kg-1 sucrose -
  - E. 0.1 mol kg-1 KCl
- As an aqueous solution of a non-volatile solute becomes more concentrated, the difference in temperature between its melting and boiling points
  - A. decreases
  - B. increases
  - C remains constant
  - D. may increase or decrease, depending on the solute
  - E. increases if the solute forms two or more ions, otherwise decreases

10.	Silver cyanide is soluble in water to the extent of $1.48 \times 10^{-6}$ mol L <sup>-1</sup> at 25°C, cyanide at 25°C is therefore:	The value of K, for silver
	. ~ (1.)	

A. 6.5 x 10-11

B: 2.2 x 10<sup>-13</sup>

C. 4.4 x 10-12

D. 3.2 x 10-12

E. none of these

# 11. As the equilibrium state of a chemical reaction is approached,

- A. The rate of the backward reaction approaches zero
- B. The rate of the forward reaction approaches zero
- C. The rates of the forward and backward reactions approach the same value

D. Both A and B are correct

### 12. A catalyst

A. may accelerate a reaction

B. affects a reaction without being consumed in the process

C. may be in same phase with the reactants or in a different phase

D.) all of these

E. none of these

### 13. Consider the reaction,

2 NOCI(g)  $\longrightarrow$  Cl<sub>2</sub>(g) + 2 NO(g), with a value A for the equilibrium constant.

If the equation were rewritten as  $NOCl(g) \longrightarrow NO(g) + 1/2 Cl_r(g)$ , the equilibrium constant for the new reaction would have the value:

A. 2A

B. A/2

C. VA

D. A2

# 14. One reason that real gases deviate from ideality is because of the

- A. existence of attractive (or repulsive) forces between molecules
- B. finite size of the gas container
- C. small non-zero mass of the container
- D. small non-zero mass of each molecule

- 15. The reaction,  $2 A + B \rightarrow C$ , is studied by monitoring the concentration of A. Over the first 3.2 minutes of observation, [A] decreases from  $6.68 \times 10^{-2} \text{ mol L}^{-1}$  to  $6.23 \times 10^{-2} \text{ mol L}^{-1}$ . Thus the average rate of this reaction over this time period is
  - A. -4.5 x 10-3 mol L-1 s-1
  - B. 1.41 x 10-3 mol L-1 s-1
  - C. 4.69 x 10-5 mol L-1 s-1
  - D. 2.34 x 10-3 mol L-1 s-1
  - E. 1.17 x 10-5 mol L-1 s-1
- 16. Reaction rates can change with
  - A. temperature
  - B. the addition of a catalyst
  - C. reactant concentrations
  - D. all of A, B, C
- 17. A solution contains 0.2 moles of A, 0.4 moles of B and 0.4 moles of C. The mole fraction of B in this solution is approximately:
  - A. 0.20
  - B. 0.22
  - C. 0.40
  - D. 0.67
  - E. 40%
- 18. For the reaction:

$$2 \text{ NOCI(g)} \rightarrow 2 \text{ NO(g)} + \text{ Cl}_2(g)$$

the kinetics will be:

- A. Second order in NOCI
- B. First order in Cl.
- C. Second order in NO
- D. All of the above
- E. Cannot predict
- 19. Which of the following has the largest mass?
  - A. 1 mole of nitrogen molecules
  - B. I mole of ammonia molecules
  - C 0.1 mole of lead atoms
  - D. I mole of fluorine atoms
  - E. I mole of methane molecules

20.	no	w many of these are sin	ong acids:				
		HCl(aq), HF(aq), HO	Cl(aq), HClO₄(aq)?				
	A.	1					
	B.	2					
	C.	3	•	•			
	D.	4					
21.	Wh	at mass of KIO, is need	ied to prepare 500.0 n	nL of a 0	0.0100 mol L <sup>-1</sup> sol	lution of KIO, ?	
	A.	2.14 g					
	В.	1.07 kg	<b>P</b>				
4	_	2.34 x 10 <sup>-3</sup> g					
1	٥.	1.07 g					
3	Ξ.	4.28 g					
22.	Wh	at is the name of the ior	whose structure is IC	2-3			
,	Ą.	iodite					
		periodite					
		hypoiodite				100	
		iodate					
		periodate					
		•				-	
23.	Wh	ich of the following co	ald be an empirical fo	rmula?			
	A.	CH.	.=			•	•
	3.	N <sub>2</sub> O <sub>5</sub> ·					
(	-	C.H.O.				7	
		all of A, B, C		7.	•		
		none of A, B, C					
							-
24.	Cor	isider the precipitation	reaction				
	2 N	(a <sub>3</sub> PO <sub>4</sub> (aq) + 3 CaC	$l_2(aq) \rightarrow 6 NaCI ($	aq) +	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> (s)		
	If C	.30 moles of Na,PO, (a (PO,), (s) which can be	q) is mixed with 0.40 obtained is:	moles of	f CaCl <sub>2</sub> (aq), the t	maximum number of	moles of
,	Α.	0.40	_		*		
	В.	0.30			ř.		
;	C.	0.20			10		
	D.	0.15	ن () چ	/ =	yG.		
	E.	0.13	2	,			
			.41				

\*4D

1,

		7		
25.	Av	ogadro's number is defined as:		
	A.	the number of carbon atoms in 12 g of 12C		
	B.			
	C.	D **		
	D.	the number of gas molecules in 22.4 L of helium gas		
	E.	none of these.		
п.	Mı	ltiple Choice (5 marks each)		
26.	The	mass percentage of oxygen in sodium perchlorate is:		
	A.	13.1 %		
	B.	52.3 %;		
	C	48.7 %;		
	D.	58.5 %;		
	E.	61.7 %;		
27.	Fro	n E' values tabulated in question 7, the standard potential for the electrochemical cell, Cu'   Fe'', Fe''   Pt is		
	A.	1.110 V		
	B.	0.430 V		
	C.	0.340 V		
	D.	0.770 V		
	E.	none of these		
28.		long will it take to plate 5.43 g of nickel onto an electrode from a solution of NiQ1, at a current of amperes?		
	A.	1447 s		
	B.	17850 s 5.		
	C.	723 s		
	D.	0.0150 s		
	E.	none of these		
29.	A 5	.42 L flask was evacuated to 2.37 x 10 <sup>-10</sup> mmHg at 75°C. How many molecules of an ideal gas ld be present in the flask under these conditions?		

A. 2.71 x 10<sup>13</sup> molecules

B. 2.22 x 10<sup>10</sup> molecules

C. 3.56 x 10<sup>10</sup> molecules

D. 2.43 x 10<sup>14</sup> molecules

E. 1.34 x 10<sup>34</sup> molecules

30. The constants in the van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

are given for NH, and CO, as

	a (L2 atm mol-2)	b (L mol-1)
NH,	4.170	0.03707
CO,	3.592	0.04267

Based on these values, which statement is the most likely to be true for the intermolecular forces and molecular size?

- A. weaker forces, larger size for NH, than CO,
- B. stronger forces, larger size for NH, than CO,
- C. stronger forces, smaller size for NH, than CO,
- D. weaker forces, smaller size for NH, than CO,

31. Consider the equilibrium.

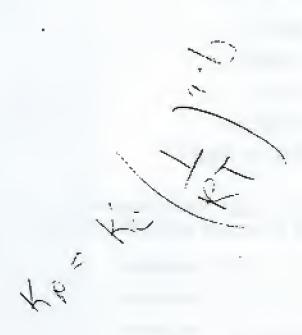
$$PCl_3(g) + Cl_2(g) \longrightarrow PCl_3(g)$$
.

At 250 °C the equilibrium partial pressures are  $P_{PCl_3} = 0.400$  atm,  $P_{Cl_2} = 0.500$  atm, and  $P_{PCl_5} = 0.0930$  atm. Therefore the equilibrium constant K for the reaction at this temperature is

- A. 2.15
  - B. 0.465
  - € 8.60

1

- D. 0.116
- E. none of these



# III. Other Questions

32. (20 marks)

a) For each substance listed below, indicate with a check mark whether it behaves as a Bronsted acid or base in dilute aqueous solutions, and give its conjugate partner.

		Acid	Base	Conjugate
(i)	hydrocyanic acid			
(ii)	fluoride ion			
(iii)	ammonia			
(iv)	acetate ion			
(v)	hydroxyl ion			

b) Predict the products of the following reaction and write a balanced net ionic equation for this reaction.

$$(NH_2)_2SO_4(aq) + NaOH(aq) \rightarrow$$

c) Balance the following oxidation-reduction (redox) reaction, occurring in basic solution:

$$PbS(s) + MnO_4^{-}(aq) \rightarrow PbSO_4(s) + MnO_4^{-2}(aq)$$

- d) Draw the best Lewis structure for the OCN-ion. (C is the central atom.)
- e) A mixture of 34.0 g of ammonia and 50.0 g of oxygen reacts according to the equation

$$4 \text{ NH}_3 + 3 \text{ O}_2 \rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O}.$$

(i) What is the limiting reagent?

(ii) How many grams of water can form?

33. (5 marks)

An adult takes about 15 breaths per minute, with each breath having a volume of 500 mL. If the air that is inhaled is "dry", but the exhaled air at 1 atm pressure is saturated with water vapor at 37 °C (body temperature), what mass of water is lost from the body during a 3 hour exam? The vapor pressure of water at 37 °C is 47.1 Torr.





# 34. (5 marks)

Calculate  $\Delta H^{\circ}$  for the reaction:  $CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + CO(NH_2)_2(s)$ 

Substance	Standard Enthalpy of formation [kJ/mol]
CO(g)	-110.53
CO <sub>2</sub> (g)	-393.51
$CO(NH_2)_2(s)$	-632
H,O( <i>l</i> )	-285.83
H <sub>2</sub> O(g)	-241.82
NH,	-46.11
NO <sub>2</sub> (aq)	-101.4
NH (aq)	-132.51
$N_2(g)$	0

35. (10 marks)
Intravenous solutions are often 5% (w/v) aqueous solutions of glucose (C<sub>s</sub>H<sub>m</sub>O<sub>s</sub>). What is the osmotic pressure of such a solution at 37 °C? Assume density of the solution is equal to 1.0 g/cm<sup>3</sup>.



36. (10 marks)

a) Write the equilibrium constant expression for the following exothermic reaction, occurring in dilute aqueous solution:

$$CaCO_3(s) + 2 HF(aq) \longrightarrow CaF_2(s) + CO_2(g) + H_2O(\ell)$$

b) Specify how the quantity of CaF<sub>2</sub> at equilibrium will change (increase, decrease or no change) if:

i) More CaCO <sub>3</sub> (s) is added to the system	
--	--

- ii) Some HF(aq) is removed
- iii) The temperature is increased
- iv) The volume is decreased
- c) Calculate the concentration of OH ions in an aqueous soluiton which has pH = 5.75.
- d) What is the equilibrium concentration of  $H_3O^*$  in a 2.0 x  $10^{-3}$  mol  $L^{-1}$  solution of hypochlorous acid  $(K_a = 3.1 \times 10^{-3})$ ?



# 37. (10 marks)

At temperature 25 °C the exothermic reaction  $NH_4^*(aq) + NO_2^*(aq) \rightarrow N_2(aq) + 2 H_2O(\ell)$  produces the following data:

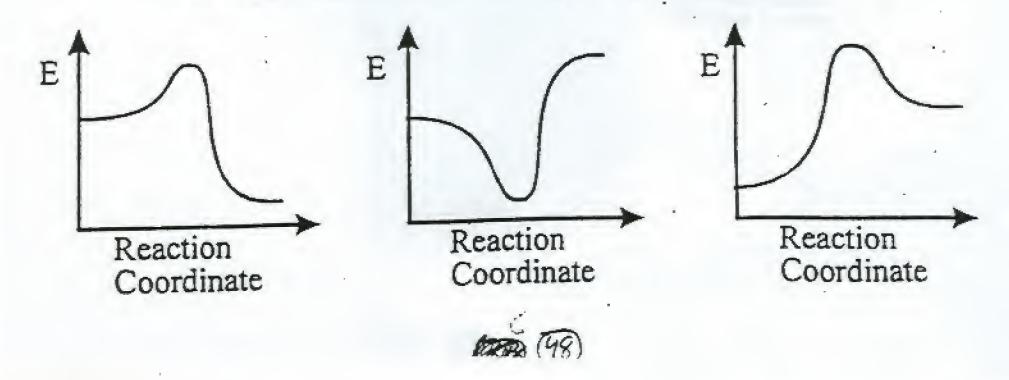
Initial Concentrations [mol L-1]		Initial Rate of Reaction [mol L <sup>-1</sup> s <sup>-1</sup> ]
NH,*(aq)	NO <sub>2</sub> -	
0.20 0.20 0.10	0.061 0.010 0.061	3.24 x 10 <sup>-6</sup> 5.3 x 10 <sup>-7</sup> 1.62 x 10 <sup>-6</sup>

a) Determine the rate law for the reaction.

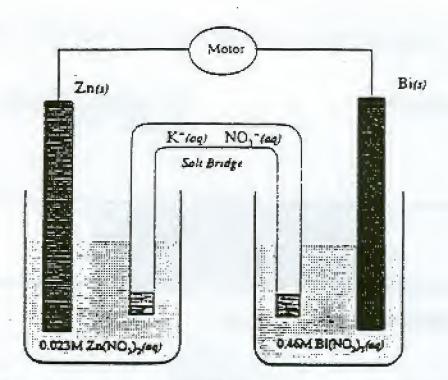
b) Determine the value of the rate constant at 25 °C, with proper units.

Spa 4 = 5

One of the diagrams below correctly represents the reaction profile for this reaction. On the correct one, indicate the distances corresponding to the activation energy, E, for the forward reaction, and the enthalpy change for the reaction. Mark the location of the activated complex on the diagram.



38. (15 marks)



A miniature electric motor was connected to the electrochemical cell shown above. After 2.5 hours operation with the motor running the mass of the Zn electrode decreased by 1.23 g.

a) Write the half-reactions for each electrode, and write the overall reaction taking place in the cell:

Anodic reaction:		
Cathodic reaction:		ar a
Overall reaction:		

- b) On the diagram above, label clearly:
  - i) the anode and the cathode;
  - ii) the polarity (+ or -) of the electrodes;
  - iii) the direction in which electrons move in the external circuit;
  - iv) the directions in which ions move in the salt bridge.
- c) Calculate the average value of the electrical current passing through the motor during the 2.5 hours of operation.

d) Calculate the cell potential using the Nernst equation (standard potentials are given below).

Half-reactions  $Bi^{3+} + 3e^{-} \rightarrow Bi$   $Zn^{2+} + 2e^{-} \rightarrow Zn$ 

E° (V) vs. SHE')
0.36
-0.76

SHE is the standard hydrogen electrode

### 39. (5 marks)

Name the strongest attractive force that contributes to the interactions between molecules or ions in the following substances, and predict which substance has the highest normal boiling point.

Substance	Predominant intermolecular force 1) -	- Highest b.p. 2)	
N <sub>2</sub>			
HF			
LiF	き I 字 A A 参数 m m mm		
. 00: - :		- :	

Notes: 1) Provide an answer for each substance.

2) Check the cell corresponding to one substance only.

THE END

